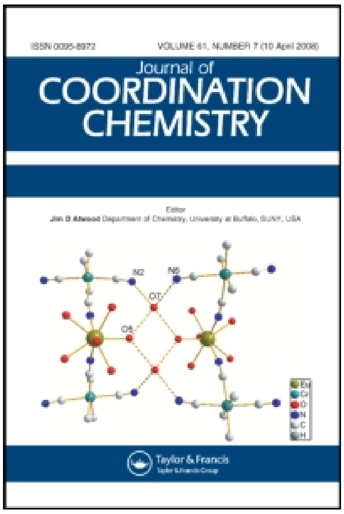

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

THE DISPLACEMENT OF BROMIDE ION BY DIMETHYL PHOSPHITE FROM THE OXOPENTABROMOMOLYBDATE(V) COMPLEX

G. Y-S. Lo[a]; Carl H. Brubaker Jr.[a]
[a] Department of Chemistry, Michigan State University, East Lansing, Michigan

To cite this Article Lo, G. Y-S. and Brubaker Jr., Carl H.(1972) 'THE DISPLACEMENT OF BROMIDE ION BY DIMETHYL PHOSPHITE FROM THE OXOPENTABROMOMOLYBDATE(V) COMPLEX', Journal of Coordination Chemistry, 2: 1, 5 — 11

To link to this Article: DOI: 10.1080/00958977208072940

URL: http://dx.doi.org/10.1080/00958977208072940

J. Coord Chem., 1972, Vol. 2, pp. 5–11

Printed in Woking, England

THE DISPLACEMENT OF BROMIDE ION BY DIMETHYL PHOSPHITE FROM THE OXOPENTABROMOMOLYBDATE(V) COMPLEX

G. Y-S. LO and CARL H. BRUBAKER, Jr.*
Department of Chemistry, Michigan State University, East Lansing, Michigan 48823

(*Received October* 1, 1971)

A study of the chemical behaviour of dimethyl phosphite, $(CH_3O)_2PO(H)$, with ammonium oxopentabromomolybdate(V), $(NH_4)_2MoOBr_5$, in the tetrahydrofuran was carried out. The stepwise substitution of the bromo ligand by dimethyl phosphite was observed by analysis of esr spectral changes. The relative concentration of each species in solutions of this reaction mixture was obtained as a function of time with the assistance of computer stimulated esr spectra by using a curvefitting program. Rate constants and activation parameters of each individual substitution step were obtained.

INTRODUCTION

Recently, Marov, *et. al.*,[1,2] reported a sequence of investigations of ligand sustitution equilibria in oxomolybdenum(V) complexes by esr spectroscopy. Similary, preliminary esr studies of diethyl phosphite substitution on molybdenum pentachloride were performed by Dalton[3] in this laboratory. The present study concerns the reaction dynamics of dimethyl phosphite substitution in oxopentabromomolybdate(V) by following changes in the esr spectrum.

EXPERIMENTAL

Materials

Dimethyl phosphite was used as obtained from Stauffer Chemical Company. Its nmr spectrum showed no impurities. Diethylamine was obtained from Mallinckrodt Chemical Works and was dried with calcium sulfate. Tetrahydrofuran was refluxed in the presence of lithium aluminium hydride and distilled immediately before use. Fisher certified phosphorous acid and hydrobromic acid (48%) were used without purification. Molybdenum pentabromide, ammonium bromide, hydrogen bromide (lecture bottle), and thionyl bromide were used as obtained from Alfa Inorganics, Matheson Coleman and Bell, Matheson Gas Products, and Research Organic/Inorganic Chemical Corp. respectively.

Ammonium Oxopentabromomolybdate(V)

The $(NH_4)_2[MoOBr_5]$ was prepared according to the reported procedure.[4] The ir spectrum of the solid product showed a strong absorption band at 975 cm $^{-1}$, the Mo–O stretching frequency. No absorption band in the region of the O–H stretching frequency was observed in the spectrum.

Anal. Calcd for $H_8Br_5MoN_2O$: Br, 72.97. Found: Br, 72.90.

The bromide was determined by potentiometric titration with standardized silver nitrate. Duplicate analyses gave identical results.

Spectroscopic Measurements

Infrared spectra were recorded by use of a Perkin-Elmer 237 B grating spectrometer. The nujol mulls were prepared in a nitrogen atmosphere box.

Nuclear magnetic resonance spectra were recorded by use of a Varian A56/60D spectrometer.

Electron spin resonance spectra were recorded by use of a Varian E-4 EPR spectrometer. The temperature of the sample compartment was kept constant through use of a Varian variable temperature controller. The spectrometer was calibrated with pitch sample.

Kinetics Measurements

All solutions for the kinetics measurements were prepared in a nitrogen glove bag. For a typical experiment, 4.50 ml of dimethyl phosphite (L) and 3.00 ml of THF were mixed well (the final [L] was 6.80 *M*) and brought to ca. 26°. Then 1.62 ml of this solution was added to 0.0732 g $(NH_4)_2[MoOBr_5]$ to give a final complex concentration, 0.083 *M*. An esr tube was filled with the solution of the reaction mixture and sealed under nitrogen. The sealed tube was placed in a water bath at 26° for ca. ten minutes and then transferred to the sample compartment (maintained at 25.9 ± 0.10) of the esr instrument. The actual temperature was measured by use of a thermocouple before and after the experiment. Esr spectra of the mixture were recorded at convenient time intervals until the reaction was ca. 90% complete. Conditions that were varied were complex concentration (0.059–0.083 *M*), dimethyl phosphite concentration (6.80–9.74 *M*), and temperature (22.2–33.3°).

Experiments that were made to find the effect of light, glass surface area, acid, or base on the rate of this reaction were carried out at 25.9°, the initial concentration of $MoOBr_4$ was 0.082 *M* and the concentration of $(CH_3O)_2PO(H)$ was 6.80 *M*. The solution of one reaction mixture was prepared and handled in the dark to study the effect of light. For the study of the effect of glass surface area, an increase in the area was accomplished by the addition of three capillary tubes (with both ends open) to the reaction solution. The surface area was estimated from the diameters and the lengths of the tubes added and the surface area in contact with the solution was increased about three-fold. Phosphorous acid, H_3PO_3, and diethylamine, $(C_2H_5)_2NH$ were used for studies of the effect of acid or base. The concentrations of added H_3PO_3 were 0.008 *M* and 0.045 *M* for two separate solutions and the concentration of $(C_2H_5)_2NH$ was 0.008 *M*.

Treatment of Esr Spectra

The line-shapes of the first derivative esr spectra of the original complex, $MoOBr_4$, and the final product, $MoOL_4$, of this reaction were determined by the comparison of the experimental spectra with calculated spectra. These spectra were synthesized by using a simple Fortran program which employed the equations[5] of both Gaussian and Lorentzian line-shapes. The three parameters ΔH_{pp} (the peak to peak width), H_0 (the position of the center of the line) and Y_m' (the maximum peak height) were measured experimentally and inserted into the program to produce theoretical esr spectra. It was found that the experimental spectra were most consistent with the Lorentzian line-shape.

The line widths of $MoOBr_4^-$ and $MoOL_4$ were measured from the experimental spectra of the pure complexes. The line widths of the mixed ligand complexes were estimated by assuming a linear change between those of $MoOBr_4^-$ and $MoOL_4$. Their values are given in Table I.

TABLE I

Line widths and g values for complexes of molybdenum(V)

Complex[a]	ΔH_{pp},[b] gauss	g
$MoOBr_4^-$	14.8	1.990 ± 0.001[c]
$MoBr_3L$	13.8	1.972 ± 0.001[c]
$MoOBr_2L_2$	12.8	1.995; 1.948 ± 0.001[c,d]
$MoOBrL_3$	11.8	1.932 ± 0.001[c]
$MoOL_4$	10.8	1.912 ± 0.001[c]
$MoOBr_4^-$	—	1.993[e]
$MoOBr_3(H_2PO_4)^-$	—	1.974[e]
$MoOBr_2(H_2PO_4)_2^-$	—	1.958; 1.950[e]
$MoOBr(H_2PO_4)_3^-$	—	1.934[e]
$MoO(H_2PO_4)_4^-$	—	1.914[e]

[a] L is the abbreviation of dimethyl phosphite. Where the charges of the complexes are uncertain they are not given.

[b] Measured and estimated as described in text.

[c] Calculated as described in text.

[d] Slight differences were observed for *cis*- and *trans*- isomers; however, since the assignment of isomers with the different values is uncertain, they are reported together as given in the Table.

[e] Ref. 10.

The theoretical esr spectrum containing several overlapping lines (Lorentzian) was simulated by a computer to give a best fit with the experimental spectrum by adjusting the two sets of parameters, H_0's and Y_m's, with a curvefitting computer program[6] in which the values of line widths, ΔHpp's, were used as constants. From these parameters, the g values and relative areas of the overlapping lines can be calculated.

The g value of $MoOL_4$ was calculated from the H_0 value which was measured from the experimental spectrum of pure $MoOL_4$ and the klystron frequency which was directly read off the dial. The g value of each of the other complexes was calculated by using the corresponding value of H_0. In each case, the H_0 value used was an average of the ten H_0 values which gave the best fit of the data in the computer similation in which the H_0 value of $MoOL_4$ was a constant (measured) value. The uncertainties of the g values (Table I) were estimated from the standard deviations of the corresponding H_0 values given by the computer outputs.

RESULTS AND DISCUSSION

The Substitution Reaction

The esr spectrum during the dimethyl phosphite substitution of Br^- in $MoOBr_4^-$ showed five distinct lines which were assigned to $MoOBr_4^-$, $MoOBr_3L$, $MoOBr_2L_2$, $MoOBrL_3$, and $MoOL_4$. Figure 1 shows several typical first derivative esr spectra of solutions of a reaction mixture as a function of time. The first spectrum (a) was recorded 22.0 minutes after the solution was prepared and consists of a strong line due to the even isotopes of Mo(I = O) and several weak lines, due mainly to the hyperfine splittings of the odd isotopes of Mo(I = 5/2). Since the intensities of the hyperfine structures are very low relative to the strong lines, they were neglected in the analysis of the kinetics. As the reaction proceeds, the intensity of the original strong line (line 1) decreased and four new lines (lines 2, 3, 4, and 5) gradually appeared as shown in Figure 1, the intensities of lines 2, 3, and 4 increased and then decreased while the intensity of line 5 constantly increased and was the only signal remaining when the reaction was completed.

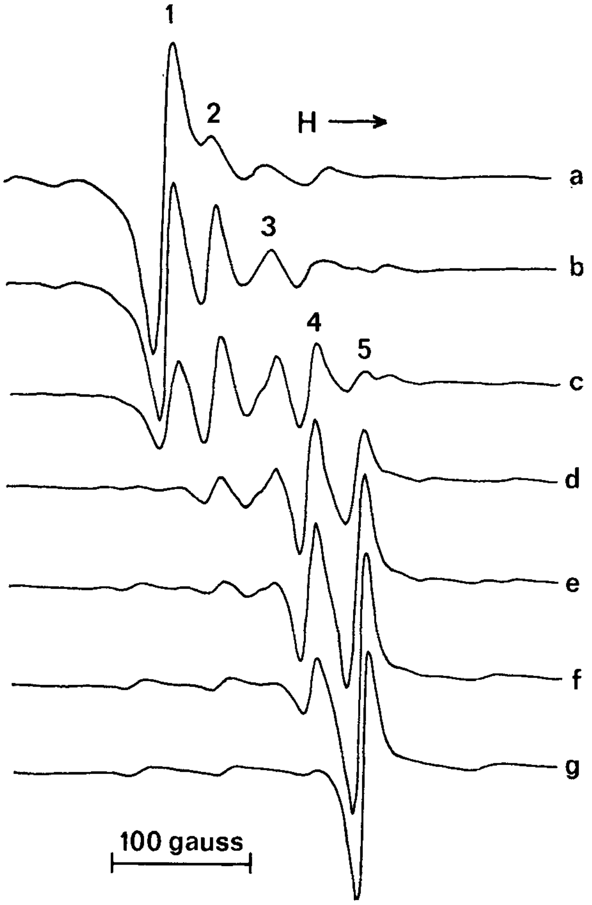

FIGURE 1 First derivative esr spectra of bromo(dimethyl phosphito) complexes of oxomolybdenum(V) recorded at various time intervals in minutes at 25.9 ± 0.1°C. (a) 22.0, (b) 80.0, (c) 136.0, (d) 185.0, (e) 236.0, (f) 310.0, (g) ~ 24 hrs.

The first line must arise from $MoOBr_4^-$ with the four bromide ligands in equatorial positions of the tetragonal structure of the complex (i.e. *cis* to the oxo ligand). It is assumed that the interaction between the *trans*-ligand and the molybdenum is very weak[3] and it may be rapidly replaced in solution by a dimethyl phosphite ligand or solvent THF, or a fast equilibrium may exist among these species. In any case, the *trans*-ligand probably does not influence the esr spectrum of the complex. Manoharan and Rogers[7] reported the study of ligand superhyperfine interactions in the esr spectra of $MoOCl_5^{2-}$ and $MoOF_5^{2-}$. They observed the fluorine superhyperfine splittings due to interactions with the four equatorial fluorines but no splitting due to the axial fluorine, thus indicating that the interaction between the axial fluorine and the molybdenum is weak. Crystal structure studies have been reported for $(C_5H_6N)_2(MoOCl_5)$[8] and $[(C_6H_5)_4As][MoOBr_4(H_2O)]$.[9] In both cases the ligands *trans* to the oxo ligand, Cl^- and H_20 respectively, appear to be at abnormally large distances from and therefore weakly bonded to the molybdenum center.

Line 5 is associated with the final product, $MoOL_4$. This interpretation is supported through the comparison with the result of the dimethyl phosphite substitution on the oxopentachloromolybdate(V) complex. It was found that the esr spectrum of the final product of the oxochloromolybdate(V) system (g = 1.913; $\Delta H_{pp} = 11.0$ gauss) closely agreed with that of the final product of the oxobromomolybdate(V) system (g = 1.942; $\Delta H_{pp} = 10.8$ gauss) while the esr spectra of the two original complexes, $MoOCl_4^-$ (g = 1.945; $\Delta H_{pp} = 8.8$ gauss) and $MoOBr_4^-$ (g = 1.990; $\Delta H_{pp} = 14.8$ gauss) are different. Therefore the final product should be primarily $MoOL_4$ and must contain none of the halide ligands. The interpretations of lines 2, 3, and 4 are straightforward. They should be the intermediate species, $MoOBr_3L$, $MoOBr_2L_2$, and $MoOBrL_3$ respectively. Line 3 consists of two closely overlapping lines which probably arise from the *cis*- and *trans*-isomers of $MoOBr_2L_2$. The above interpretations are in good agreement with the work of Marov, *et.al.*,[10] on the oxobromo(phosphato)molydbate(V) complexes. The comparison of the g values of the two systems are given in Table I.

Esr spectra of $MoOL_4$ were recorded at ten degree temperature intervals from 20 to −160° and no phosphorus superhyperfine splitting was observed in any of these spectra which suggests that the phosphorus atom may not be bound to molybdenum. A qualitative study was made of the dimethyl methylphosphonate, $(CH_3O)_2P(O)CH_3$, substitution on the $MoOBr_4^-$ complex. It gave the same series of esr spectra as the dimethyl phosphite. Since the $(CH_3O)_2P(O)CH_3$ ligand must be bound to the molybdenum through oxygen, it is suggested that the $(CH_3O)_2PO(H)$ ligand is similarly bound. The g values of the oxobromo(dimethyl phosphito)-molybdate(V) complexes are in good agreement with those of the oxobromo(phosphato)molybdate(V) complexes reported by Marov, *et. al.*,[10] where the phosphate ligand is also bound through oxygen. However, the possibility of the phosphorus in dimethyl phosphite being bound to the molybdenum cannot be definitely ruled out. Attempts to isolate the final product were without success. Since no direct evidence has been obtained, the charges of the complexes (except $MoOBr_4^-$) are uncertain.

The substitution reactions were studied in the presence of excess dimethyl phosphite and the concentration range was 6.80–9.74 *M*. The complex apparently forms dimers at low concentration of dimethyl phosphite as suggested by esr evidence similar to that of previous studies.[10] The range of complex concentrations used was $5.9–8.3 \times 10^{-2}$ *M*. This was limited by its solubility and the desired intensities of the esr signals.

Determination of Relative Concentrations

The relative concentration (or mole fraction, X_1) of each species in the reaction solution was obtained as a function of time from esr spectra. The line area, A, of each species' contribution to the total spectrum for a first derivative Lorentzian line-shape can be calculated from the equation

$$A = \frac{2\pi}{3^{1/2}} Y_m'(\Delta H_{pp})^2$$

if Y_m' and ΔH_{pp} are known. This area should be proportional to the number of unpaired spins and therefore the concentration of the paramagnetic species in the sample. The A_1 values for each species were calculated from the values of ΔH_{pp} and Y_m' which were obtained as a function of time from the computer simulated esr spectra. Values of X_i were then calculated from the equation

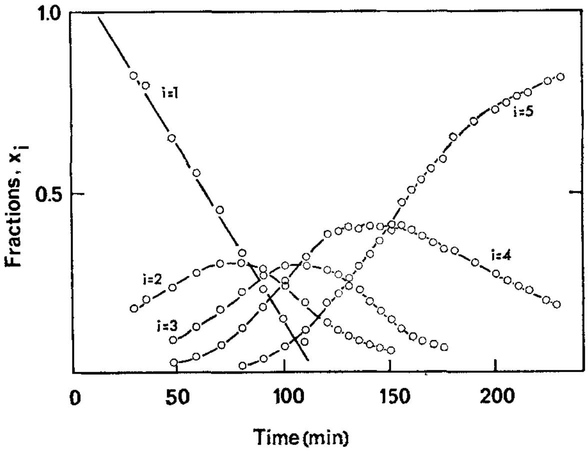

FIGURE 2 Plot of fractions *vs.* time for the reaction of $MoOBr_4^-$ with $(CH_3O)_2PO(H)$ in THF at 29.6°. The total Mo(V) concentration is 0.082 *M* and the $(CH_3O)_2PO(H)$ concentration is 6.80 *M*.

$$X_i = \frac{N}{\sum_{i=1}^{N} A_i};$$

$N = 2–5$ with the assumption that the total concentration of Mo(V) in the solution was constant and completely contained in the five species at all times during the reaction. This was supported by the fact that with the same instrumental conditions the intensity of $MoOL_4$ when the reaction was complete was almost the same as the intensity of $MoOBr_4^-$ at the beginning of the reaction. A typical plot of fractions *vs.* time is shown in Figure 2.

Analysis of Kinetics

The overall substitution reaction of Br^- in $MoOBr_4^-$ by $(CH_3O)_2PO(H)$, L, consists of four individual steps. Each of these steps can be expressed by the general equation, $M_i + L \xrightarrow{k_i'}$

$M_{i+1} + Br^-$, i = 1–4, where M_1, M_2, M_3, M_4 and M_5 represent $MoOBr_4^-$, $MoOBr_3L$, $MoOBr_2L_2$, $MoOBrL_3$, and $MoOL_4$ respectively with the assumption that the reverse reactions are insignificant under the experimental conditions. The first step has an apparent zero-order rate law and the remaining steps have apparent first-order rate laws. Pseudo zero-and first-order results because $(CH_3O)_pPO(H)$ is always in large excess. Their mathematical forms are given in the following simultaneous equations.

$$d[M_1]/dt = - k_1 \quad (1)$$

$$d[M_2]/dt = k_1 - k_2 [M_2] \quad (2)$$

$$d[M_3]/\mathrm{dt} = k_2[M_2] - k_3 [M_3] \quad (3)$$

$$d[M_4]/dt = k_3[M_3] - k_4[M_4] \quad (4)$$

$$d[M_5]/dt = k_4[M_4] \quad (5)$$

where $k_1' = k_1/[Mo(V)][L]$, $[Mo(V)]$ is the initial concentration of $MoOBr_4^-$; $k_i' = k_i/[L]$ $i = 2$–4. Equation (2) became $d[M_2]/dt = - k_2[M_2]$ after all of M_1 had been consumed.

Exhibiting zero-order behaviour, a plot of X_1 *vs.* time gave a straight line. After all of M_1 had been consumed a plot of ln X_2 *vs.* time gave good linearity indicating a change to a first-order reaction. The last two reaction steps also showed first-order behaviour in complex concentration since, after all of the preceding species had been consumed, straight lines were obtained from plots of ln X_3 and ln X_4 *vs.* time. Uncertainties in X_i were calculated from the Y_m' standard deviations, estimated statistically by the computer program used to stimulate the esr spectra. The uncertainties for X_1 are less than 10%, for X_2 and X_4 are less than 7%, and for X_3 are less than 20%.

Apparent rate constants for each step of this reaction were determined graphically and by a least-squares treatment with good agreement by using a small portion of X_i values. They were also found by using a computer program[6] which adjusts the four rate constants in the five simultaneous rate law equations to give a best fit with all the experimental values of X_i. The observed and

TABLE II

Rate constants for the first substitution step, $MoOBr_4^-$ to $MoOBr_3L$

Temp., °C	[Mo],[a]M	[L],[a]M	10^5k_1,[b]mol. l^{-1}. sec^{-1}	10^5k_1,[b,c]1. mol^{-1}. sec^{-1}	10^5k_1,[d,e] mol. 1^{-1} sec^{-1}	10^5k_1,[d,e,c] 1. mol^{-1}. sec^{-1}
33.3	0.082	6.80	2.00 ± 0.04	3.58 ± 0.08	2.02 ± 0.15	3 63 ± 0.27
29.6	0.082	6.80	1.31 ± 0.03	2.35 ± 0.05	1.38 ± 0.16	2.47 ± 0.29
22.2	0.082	6.80	0.56 ± 0.01	1.01 ± 0.02	0.60 ± 0.06	1.08 ± 0.10
25.9	0.083	6.80	0.89 ± 0.02	1.57 ± 0.03	0.92 ± 0.07	1.62 ± 0.12
25.9	0.070	6.80	0.76 ± 0.03	1.60 ± 0.05	0.98 ± 0.09	2.06 ± 0.20
25.9	0.059	6.80	0.61 ± 0.02	1.52 ± 0.05	0.67 ± 0.10	0.67 ± 0.24
25.9	0.082	8.39	0.92 ± 0.03	1.33 ± 0.04	1.01 ± 0.08	1.47 ± 0.11
26.0	0.083	9.74	1.05 ± 0.03	1.30 ± 0.04	1.22 ± 0.12	1.51 ± 0.15

Footnotes to Tables II—V

[a] [Mo] is the initial concentration of $MoOBr_4^-$; [L] is the concentration of $(CH_3O)_2PO(H)$.

[b] Observed zero-order constant, k_1, obtained by least-squares treatment where simple rate law $-d[MoOBr_4^-]/\mathrm{dt} = k_1$ apply.

[c] $k_1l = k_1/[Mo]\,[L]$

[d] Observed rate constants obtained from the treatment of the five simultaneous rate law equations by use of a computer program. Their uncertainties were estimated statistically by the computer program.

[e] Zero-order constant, k^1

[f] Observed first-roder constants, ki, obtained by least-squares treatment where simple rate law $-d[M_i]/dt = k_i[M_i]$ apply.

[g] $i = 2$; $[M_2]$ is the concentration of $MoOBr_3L$.

[h] Calculated from the rate law $-d[M_i]/dt = k_i'[M_i]\,[L]$, $k_i' = k_i/[L]$.

[i] First-order constant, k_3.

[j] $i = 3$; $[M_3]$ is the concentration of $MoOBr_2L_2$.

[k] First-order constant, k_3'

[l] $i = 4$; $[M_4]$ is the concentration of $MoOBrL_3$.

[m] First-order constant, k_4.

TABLE III

Rate constants for the substitution step, $MoOBr_3L$ to $MoOBr_2L_2$

Temp.,°C	[Mo],^{a}M	[L],^{a}M	$10^4K_2,^{f,g}sec^{-1}$	$10^5k_2,^{f,g,h}$ $l.mol^{-1}.sec^{-1}$	$10^4k_2,^{d,i}sec^{-1}$	$10^5k_2,,^{d,i,h,g}$ $l.mol^{-1}.sec^{-1}$
33.3	0.082	6.80	6.82 ± 0.48	10.03 ± 0.71	10.7 ± 1.5	15.7 ± 2.2
29.6	0.082	6.80	5.07 ± 0.15	7.45 ± 0.22	7.5 ± 2.1	11.0 ± 3.0
22.2	0.082	6.80	2.13 ± 0.07	3.14 ± 0.10	2.80 ± 0.40	4.12 ± 0.59
25.9	0.083	6.80	3.45 ± 0.08	5.07 ± 0.12	5.18 ± 0.72	7.6 ± 1.1
25.9	0.070	6.80	4.25 ± 0.28	6.25 ± 0.41	4.77 ± 0.88	7.0 ± 1.3
25.9	0.059	6.80	3.60 ± 0.95	5.29 ± 1.39	4.8 ± 1.0	7.1 ± 1.5
25.9	0.082	8.39	3.98 ± 0.17	4.75 ± 0.20	4.8 ± 1.0	5.7 ± 1.2
26.0	0.083	9.74	5.23 ± 0.28	5.37 ± 0.29	6.3 ± 1.8	6.4 ± 1.8

TABLE IV

Rate constants for the substitution step, $MoOBr_2L_2$ to $MoOBrL_3$

Temp.,°C	[Mo],^{a}M	[L],^{a}M	$10^4k_3,^{f,j}sec^{-1}$	$10^5k_3,^{f,j,h}$ $l.mol^{-1}.sec^{-1}$	$10^4k_3,^{d,k}sec^{-1}$	$10^5k_3,^{d,k,h,j}$ $l.mol^{-1}.sec^{-1}$
33.3	0.082	6.80	—	—	8.8 ± 1.5	12.9 ± 2.1
29.6	0.082	6.80	4.52 ± 0.43	6.64 ± 0.63	5.8 ± 1.8	8.5 ± 2.6
22.2	0.082	6.80	1.97 ± 0.08	2.89 ± 0.12	2.52 ± 0.53	3.70 ± 0.78
25.9	0.083	6.80	2.83 ± 0.80	4.2 ± 1.2	4.13 ± 0.52	6.08 ± 0.76
25.9	0.070	6.80	3.82 ± 0.28	5.61 ± 0.41	5.0 ± 0.41	7.3 ± 1.9
25.9	0.059	6.80	3.30 ± 0.30	4.85 ± 0.44	4.5 ± 1.2	6.6 ± 1.7
25.9	0.082	8.39	3.62 ± 0.73	4.31 ± 0.87	4.8 ± 1.2	5.7 ± 1.4
26.0	0.083	0.83	5.33 ± 0.53	5.48 ± 0.54	6.0 ± 2.0	6.1 ± 2.0

TABLE V

Rate constants for the last substitution step, $MoOBrL_3$ to $MoOL_4$

Temp.,°C	[Mo],^{a}M	[L],^{a}M	$10^4k_4,^{f,l}sec^{-1}$	$10^5k_4,,^{f,l,h}$ $l.mol–^1.sec–^1$	$10^4k_4,^{d,m}sec–1$	$10^5k_4,,^{d,m,h,l}$ $l.mol–^1.sec–^1$
33.3	0.082	6.80	3.34 ± 0.03	4.91 ± 0.05	4.32 ± 0.45	6.35 ± 0.66
29.6	0.082	6.80	2.05 ± 0.03	3.01 ± 0.03	2.60 ± 0.55	3.82 ± 0.81
22.0	0.082	6.80	0.91 ± 0.01	1.33 ± 0.02	1.16 ± 0.18	1.70 ± 0.26
25.9	0.083	6.80	1.39 ± 0.02	2.05 ± 0.03	1.83 ± 0.13	2.70 ± 0.19
25.9	0.070	6.80	1.52 ± 0.04	2.23 ± 0.06	2.20 ± 0.42	3.24 ± 0.62
25.9	0.059	6.80	1.53 ± 0.02	2.25 ± 0.03	1.95 ± 0.27	2.87 ± 0.40
25.9	0.082	8.39	1.60 ± 0.03	1.91 ± 0.04	2.10 ± 0.30	2.50 ± 0.36
26.0	0.083	9.74	1.99 ± 0.03	2.04 ± 0.03	2.68 ± 0.40	2.76 ± 0.41

calculated rate constants, k_i and k_i', obtained from both methods for each substitution step are given in Tables II–V. Values of k_1 obtained from the two methods are in good agreement; whereas values of k_2, k_3, and k_4 obtained from the treatment of the five simultaneous equations are systematically higher than those obtained by the least-squares treatment of partial data. The rate constants obtained from the computer anaylsis should be more realistic than those obtained by a least-squares treatment of partial data, since all values of X_1 were used. The rather high uncertainties are not surprising for such a complex system considering the difficulties described for the data treatment.

TABLE VI.

Values of activation parameters for the substitution steps, $M_i + L \xrightarrow{k'_i} M_{i+1} + Br^-$, $i = 1\text{–}4$

Substitution Step	E, Kcal.mol^{-1}	log$_{10}$A[a]	$\Delta H^{\ddagger}_{298}$, Kcal.mol^{-1}	$\Delta S^{\ddagger}_{298}$, cal. deg^{-1}.mol^{-1}
$MoOBr_4$ to $MoOBr_3L$	19.0 ± 1.8	9.1 ± 1.3	18.4 ± 1.3	−18.9 ± 5.9
$MoOBr_3L$ to $MoOBr_2L_2$	21.2 ± 1.1	11.3 ± 1.1	20.6 ± 1.1	−8.8 ± 3.7
$MoOBr_2L_2$ to $MoOBrL_3$	18.7 ± 2.0	9.5 ± 1.5	18.1 ± 2.0	−17.0 ± 6.9
$MoOBrL_3$ to $MoOL_4$	20.0 ± 1.7	10.0 ± 1.7	19.4 ± 1.7	−14.7 ± 5.9

[a] Log$_{10}$A (A is preexponential factor in 1.mol^{-1}.sec^{-1}) was calculated by using a rate constant at 25° found from extrapolation.

The first substitution step is first-order with respect to L and zero-order with respect to $MoOBr_4^-$, yet the rate does depend on the initial concentration of $MoOBr_4^-$.

Studies were made to find the effect of light, glass surface area, acid, or base on the rate of this reaction in an effort to gain some understanding of the behaviour of this first substitution step. The above factors have no significant effect on the rate of this reaction. Attempts to derive a complex rate law to fit the observed behaviour were made without success. At this time, no reasonable explanation is apparent for the anomalous zero-order rate law and dependence of rate on initial concentration of complex.

The remaining substitution steps have mixed second-order rate laws (*i.e.* first-order with respect to the corresponding complex and first-order with respect to L), and so may be second-order displacement reactions.

Plots of $-\ln k_i'$, $i = 1\text{–}4$ *vs.* $1/T$°K for the four individual substitution steps were made from the first six k_i' values in the last column of Tables II–V respectively. The graphs were linear within experimental error. The seventh and eighth solutions were studied at much higher $(CH_3O)_2PO(H)$ concentrations, which amounts to a significant solvent change, and therefore they are not included in determining activation energy, etc. The activation energy, E_a, and its uncertainty were obtained from a least–squares treatment of these six points. Then the other activation parameters, $\log_{10} A$, $\Delta H^{\ddagger}_{298}$, and $\Delta S^{\ddagger}_{298}$, were calculated (Table VI).

ACKNOWLEDGMENT

The authors are grateful to Professor James L. Dye for his helpful discussions and the use of his computer program. Financial support from the National Science Foundation under GP–7088X and 17422X is also acknowledged.

BIBLIOGRAPHY

1. I. N. Marov, Yu. N. Dubrov, V. K. Belyaeva, A. N. Ermakov, and D. I. Ryabchikov, *Russ. J. Inorg. Chem.* **11,** 1311 (1966).
2. I. N. Marov, V. K. Belyaeva, A. N. Ermakov, and Yu. N. Dubrov, *Russ. J. Inorg. Chem.* **14,** 1391 (1969).
3. L. A. Dalton, M. S. Thesis, Michigan State University, East Lansing, Michigan, 1967.
4. E. A. Allen, B. J. Brisdon, D. A. Edwards, G. W. A. Fowles, and R. G. Williams, *J. Chem. Soc.* 4649 (1963).
5. C. P. Poole, Jr., "Electron Spin Resonance", Interscience Publishers, New York, 1967, Ch. 20.
6. J. L. Dye and V. A. Nicely, *J. Chem. Ed.* **48,** 443 (1971).
7. R. T. Manoharan and M. T. Rogers, *J. Chem. Phys.* **49,** 5510 (1068).
8. J. C. Sheldon, Proceedings of the XII International Conference on Coordination Chemistry, Sydney, 1969
9. J. G. Scan, *Acta Cryst.* **23,** 85 (1967).
10. I. N. Marov, Yu. N. Dubrov, V. K. Belyaeva, and A. N. Ermakov, *Russ. J. Inorg. Chem.* **13,** 1107 (1968).